

PATENT SPECIFICATION

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(54) ALUMINA COMPOSITIONS

(71) We, W. R. GRACE & CO, a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of Grace Plaza, 1114 Avenue of the Americas, New York, New York 10036, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel materials that can be used for making catalysts.

A common form of catalyst consists of a solid support and a catalytic material carried on the support; the solid support is then usually particles of a porous material—e.g. alumina. The particles are typically of a size equal to spherical particles 1 mm in diameter up to 15 mm in diameter. The porous material—e.g. alumina—may need to be shaped into particle form—e.g. spheres, spheroids, pills, cylinders—and we will refer to the material before it is shaped as “support material” and after it is shaped as “formed support”. The novel alumina monohydrate of this invention and its admixture with amorphous alumina are in this sense a support material; the microspheroidal particles, whether made from the support material of this invention or from a similar material, are in this sense a formed support; and these microspheroids when loaded with a catalytic agent are a catalyst.

The activity, efficiency, stability, and durability of a catalyst in a reaction depend upon the chemical, physical, and structural properties of the catalyst precursors, i.e., the support material and the formed support particles, and the nature and distribution of the catalytic material on the formed support. Minor variations in these properties may produce substantial differences in the performance of the catalyst. Desirably, the properties of the support material that enhance catalytic activity are retained by the formed support particles. In general, the formed support and catalyst comprising small amounts of the catalytic material on the support have essentially the same physical and structural properties with slight differences due to the effects of the thermal activation of the catalyst.

The internal porous structure of the catalyst particles and their precursors determines the extent and accessibility of surface area available for contact of the catalytic materials and the reactants. Increased pore size results in greater diffusion rates for reactants and products in and out of the catalyst particles and this often results in improved catalyst activity. However, the extent to which pore size can be advantageously increased is limited. As the pore size is increased, there is a decrease in the surface area where the reactions take place. A good catalyst should have a balanced combination of high specific surface area, cumulative pore volume, and macroporosity. High macroporosity means a pore size distribution with a relatively high proportion of pores having a diameter greater than 1000Å. Further, alumina and formed alumina with a low density and consequent low thermal inertia will produce a catalyst that will reach reaction temperatures sooner.

Catalyst support material is frequent a porous refractory inorganic oxide, such as silica, alumina, magnesia, zirconia, titania, and combinations thereof. Alumina is a particularly desirable support material since it inherently has a high degree of porosity and will maintain a comparatively high surface area over the temperature range normally encountered in many catalytic reactions. However, when used

under high temperature conditions for long periods of time, overheating of the alumina may cause sintering and change in the crystalline phase of the alumina which reduce catalytic activity, for example, due to loss of surface area available for catalysis. Alumina is used as a catalyst support in the form of a finely divided powder or of macrosized particles formed from a powder.

Since the physical and chemical properties of alumina are highly dependent on the procedures followed in its preparation, many preparation processes have been developed in attempts to optimize its properties for use as a catalyst support material. Alumina is frequently precipitated by combining a water-soluble, acidic aluminum compound which may be an aluminum salt such as aluminum sulfate, aluminum nitrate, or aluminum chloride, and an alkali metal aluminate such as sodium or potassium aluminate. However, the properties of the resultant compositions after washing and drying have generally been deficient in one or more of the properties of high surface area, macroporosity, phase stability, and low density.

Typical methods of making alumina with some of the characteristics desired of a support material are disclosed in U.S. Patents 2,988,520, 3,520,654, 3,032,514 and 3,124,418. U.S. Patent 3,864,461 is particularly interesting as it discloses the production of a crystalline alumina of low bulk density which is identified by its x-ray bands as identical to pseudoboehmite, in some cases in admixture with a small amount of bayerite.

In addition to retaining the surface area, porosity, and density characteristics of the starting alumina material, a process for the formation of macrosized alumina particles should produce formed alumina with low shrinkage and high attrition resistance and crush strength. Conventional low density supports are generally deficient in structural integrity. Unless stabilized, an alumina particle will undergo considerable shrinkage of its geometric volume when exposed to high temperatures during use. Excessive shrinkage produces unoccupied channels in the catalyst bed through which reactants pass without contact with the catalyst.

High attrition resistance provides structural integrity and retention of activity under conditions of mechanical stress. During transfer, loading into the reaction zone, and prolonged use, the catalyst particles are subjected to many collisions which result in loss of material from the outer layers. Attrition of the catalytically active layer present in the outer volume of the particles affects catalytic performance and also results in a decrease of the volume of the material in the reaction zone. Volume loss by shrinkage and/or attrition of the highly compacted, tightly held particles in a fixed catalyst bed tends to loosen them and allow for increased motion and collisions during vibration. Once a packed bed becomes loose, attrition tends to increase. During storage, the catalyst is often packed in large tall containers awaiting loading. In order to withstand the forces generated by the weight of the particles above them, the catalyst must exhibit high crush strength.

The size, size distribution, and shape of the particles affect both structural integrity and catalytic activity. These properties determine the volume of catalyst that can be packed in a fixed bed, the pressure drop across the bed, and the outer surface area available for contact with the reactants. Finely divided alumina may be pelletized, tabletized, molded or extruded into macrosized particles of the desired size and shape. Typically, the macrosized particles are cylinders of diameter about 1/32 to 1/4 inch and a length to diameter ratio of about 1:1 to 3:1. Other shapes include spheroidal, polylobal, figure-eight, clover leaf, dumbbell and the like.

Spheroids offer numerous advantages as a catalyst support over particles having angular shaped surfaces with salients or irregularities, such as extruded cylinders. Spheroidally shaped particles permit a more uniform packing of the catalyst bed, thereby reducing variations in the pressure drop through the bed and in turn reducing channelling which would result in a portion of the bed being bypassed. Another advantage in using particles of this shape is that the spheroids exhibit no sharp edges which will attrit during processing, transfer, or use.

One of the most described methods for producing spheroidal alumina particles is the oil-drop method in which drops of an aqueous acidic alumina material gel to spheroids in falling through a water-immiscible liquid and coagulate under basic pH conditions. A wide variety of oil-drop techniques have been developed in attempts to provide structural and mechanical properties that would enhance the activity and durability of alumina-supported catalysts. The density, surface area, porosity and uniformity of the spheroidal product vary greatly with the nature of the alumina feed and, along with crush strength and attrition resistance, are dependent

on the conditions used in the preparation of the feed and the coagulation and gelation steps, as well as subsequent drying and calcination steps. Internal gelation, i.e. gelation of the alumina by a weak base, such as hexamethylenetetramine, that is added to the feed before drop formation and that releases ammonia in the heated immiscible liquid, is the most common oil-drop method.

United States Patent No. 3,558,508 to Keith et al. describes an oil-drop method employing an external gelation technique in which gaseous ammonia is introduced into the bottom of a column containing the water-immiscible liquid and coagulates the droplets by contacting their external surfaces. The Keith et al. process is based to a considerable extent on the use of specific alumina feed prepared by acidic hydrolysis of finely divided aluminum. Spherical alumina particles may also be formed by the hydrocarbon/ammonia process described in Olechowsak et al., "Preparation of Spherically Shaped Alumina Oxide", *International Chemical Engineering*, Volume 14, No. 1, pages 90-93, January, 1974. In this process, droplets of a slurry of nitric acid and dehydrated aluminum hydroxide fall through air into a column containing hydrocarbon and ammonia phases. The droplets assume spheroidal shapes in passing through the water-immiscible liquid and then are coagulated to firm spheroidal beads or pellets in the coagulating medium. Similar processes utilizing pseudosol feeds and hydrochloric acid are described in:

1. Katsobashvili et al., "Formation of Spherical Alumina and Aluminum Oxide Catalysts by the Hydrocarbon-Ammonia Process—1. The Role of Electrolytes in the Formation Process", *Kolloidnyi Zhurnal*, Vol. 28, No. 1, pp. 46-50, January-February, 1966;

2. Katsobashvili et al., "Preparation of Mechanically Strong Alumina and Aluminum Oxide Catalysts in the Form of Spherical Granules by the Hydrocarbon-Ammonia Forming Method", *Zhurnal Prikladnoi Khimii*, Vol. 39, No. 11, pp. 2424-2429, November, 1966; and

3. Katsobashvili et al., "Formation of Spherical Alumina and Aluminum Oxide Catalysts by the Hydrocarbon-Ammonia Process—Coagulation Structure Formation During the Forming Process", *Kolloidnyi Zhurnal*, Vol. 29, No. 4, pp. 503-508, July-August, 1967.

Catalysts are used to convert pollutants in automotive exhaust gases to less objectionable materials. Noble metals may be used as the principal catalytic components or may be present in small amounts to promote the activity of base metal systems. United States Patents Nos. 3,189,563 to Huel and 3,932,309 to Graham et al. show the use of noble metal catalysts for the control of automotive exhaust emissions. United States Patent No. 3,455,843 to Briggs et al. is typical of a base metal catalyst system promoted with noble metal. Unpromoted base metal catalysts have been described in United States Patent No. 3,322,491 by Barrett et al.

The activity and durability of an automotive exhaust catalyst is in part dependent on the location and distribution of noble metals on the support. Since the use of noble metal is controlled to a great extent by cost, small amounts of noble metals should be placed on the support in a manner that achieves the best overall performance over the life of the catalyst.

Several competing phenomena are involved in the surface treatment. Impregnating the maximum amount of the support particle provides the greatest amount of impregnated surface area. However, since gas velocities are high and contact times are short in an automotive exhaust system, the rate of oxidation of carbon monoxide and hydrocarbons and the reduction of nitrogen oxides are diffusion controlled. Thus, the depth of impregnation should not exceed the distance that reactants can effectively diffuse into the pore structure of the particle. A balance of impregnated surface area coupled with proper dispersion and accessibility should be achieved to formulate a practical catalyst.

Catalytic metal accessibility and dispersion will provide initial high catalytic activity, once the catalyst reaches operating temperature. However, since significantly high amounts of hydrocarbons, carbon monoxide, and other partially combusted materials are produced in exhaust gases during the initial moments of the engine start, the catalyst should have low thermal inertia in order to operate efficiently when the reaction zone is at a relatively low temperature.

A common deficiency of exhaust catalysts is decreased activity when exposed to high temperatures, mechanical vibration and poisons present in the exhaust such as lead, phosphorus, sulfur compounds, etc., for long periods of use of up to 50,000 miles or so. An effective catalyst will retain its activity through resistance to noble

metal crystallite growth, poisons, crystalline phase changes, and physical degradation.

5 An optimum high temperature alumina catalyst support has low density and high macroporosity while retaining substantial surface area and crush strength and attrition resistance. Furthermore, it is stable in crystalline phases and geometric volume occupied. Difficulties have been encountered in achieving the proper balance of these interrelated and sometimes competing properties and in combining an alumina support and metal impregnation techniques to provide a catalytic converter capable of decreasing automotive exhaust emissions to the levels required by present and future government standards.

10 We have now found a novel, crystalline, alumina monohydrate which can be converted to a formed support having a unique and valuable combination of desirable properties.

15 According to the present invention there is provided an alumina composition comprising a boehmite - pseudoboehmite intermediate, said composition having a [020] d-spacing of about 6.2 to about 6.4Å and a mid-point width of X-ray diffraction peak [020]d of about 1.65 to about 1.85Å and requiring from about 130 to about 180 milliequivalents of sulfuric acid per mole of alumina to change the pH of a water slurry of the composition from about 8.3 to about 4.0.

20 For making a formed support, this boehmite - pseudoboehmite intermediate should be in admixture with a minor amount of alumina gel, so that about 70 to 85% of total alumina in the mixture is in crystalline form. Such a mixture is part of our invention.

25 This alumina composition having properties particularly suitable for the formation of spheroidal particles having the combination by a process in which the alumina is precipitated under specific and controlled reactant concentrations, and reaction temperature, time, and pH and aged at a higher pH. The rate of addition of reactants can be controlled to give the desired balance of crystalline amorphous alumina in a mixture.

30 In particular the composition can be prepared by a process which comprises the following steps:

1. An aqueous solution of an aluminium salt, generally of a strong mineral acid, preferably aluminium sulfate, having an Al_2O_3 concentration of 5 to 9 weight percent and at a temperature of 130 to 160°F, is added to water at a temperature of 140 to 170°F; the amount of aluminium salt added is sufficient to adjust the pH of the mixture to 2 to 5;

35 2. An aqueous solution of sodium aluminate (or other alkali metal aluminate) having an Al_2O_3 concentration in excess of 16, typically 18 to 22, weight percent and a temperature of 130 to 160°F, and a further amount of aqueous aluminium sulfate (or other aluminium salt) solution are simultaneously (but separately) added to the mixture—this precipitates alumina to form an alumina slurry. Addition of alkali metal aluminate raises the pH of the mixture to a value in the approximate region pH 7 to pH 8, and the pH of the slurry is maintained during the precipitation from 7 to 8 and the temperature is kept at from 140 to 180°F, and a rate of addition of the solution is maintained during the precipitation to form intermediate boehmite - pseudoboehmite alumina;

45 3. The pH of the slurry is then adjusted to 9.5 to 10.5. The slurry may then, optionally, be aged and the slurry is then filtered and the filter cake washed to provide a substantially pure alumina.

50 This process is described and claimed in our Application No. 11808/78, Serial No. 1603461.

The process is reproducible and prepares a hydrous alumina from which process impurities can be easily removed by water washing and filtration. The control of temperature, time rates, concentrations and pH produce an alumina which is substantially pure (as defined below), microcrystalline pseudoboehmite - boehmite intermediate generally having from 70 to 85 weight percent of the total amount of Al_2O_3 present in crystalline form.

55 Substantially uniform spheroidal alumina particles having an unexpected combination of low density and high surface area, macroporosity, phase stability, and mechanical strength can be prepared from the wet or dried boehmite - pseudoboehmite intermediate as described and claimed in our Application No. 8029047, Serial No. 1603463. A slurry of alumina is prepared in an acidic aqueous medium and droplets of the slurry are passed through air into a column containing an upper body of a water-immiscible liquid and ammonia and a lower body of aqueous alkaline coagulating agent. The resulting spheroidal particles are aged in

aqueous ammonia to the desired hardness. The aged particles are dried and calcined.

It has also been discovered that a catalyst comprising a catalytically active metal or metal compound impregnated on these spheroidal alumina particles has excellent activity and durability in many catalytic systems. It is especially suited for eliminating pollutants in automotive exhaust streams because of its quick light off and sustained activity under high temperatures and mechanical vibrations present in exhaust systems.

The process for preparing the alumina of this invention comprises five main phases. Phase I involves the formation of boehmite crystal seeds at acidic pH's in very dilute aqueous systems and is referred to as the nucleation phase.

Phase II, which is the main phase, involves the precipitation and crystallization of alumina at a pH from 7 to 8. During this phase, crystallites of boehmite or pseudoboehmite grow from the hydrous precipitated alumina onto the crystalline seeds. Phase II is called the precipitation and crystallite growth phase.

Phase III involves changing the pH of the system by the addition of an alkaline solution in order to reduce the electrical surface charge on the alumina precipitate. During this phase, the positive charge of the alumina particles is gradually reduced until at pH 9.4—9.6, it becomes essentially zero. In this condition, the alumina precipitate is said to exist at its isoelectric point. That is the point in pH at which the surface does not exhibit any electrical charge. Phase III is, therefore, called the surface electrical charge reduction phase.

Optional Phase IV involves the aging of the system for predetermined periods of time, and phase V involves the filtering and washing of the resulting slurry in order to remove undesirable electrolytes or impurities.

An optional final step of the process is the drying of the washed filter cake to a powdery material. This may be done with or without the incorporation of specific additives in order to reduce the absorption of impurities.

The reactants used to carry out the process of this invention are water soluble aluminum salts, such as aluminum sulfate, aluminum nitrate, aluminum chloride, and the like; and an alkali metal aluminate, such as sodium aluminate, potassium aluminate, and the like. In specific embodiments, the preferred reactants are aluminum sulfate and sodium aluminate for reasons of cost, availability, and desirable properties in carrying out the invention. The reactants are used in the form of aqueous solutions. The aluminum sulfate may be used over a wide range of concentrations above about 5 weight percent; however, for practical reasons, it is used preferably in high concentrations from about 6 to about 8 wt. % equivalent Al_2O_3 .

The sodium aluminate solution should be a relatively freshly prepared solution exhibiting no precipitated or undissolved alumina. The sodium aluminate may be characterized by its purity and equivalent alumina concentration, which should be in excess of 16 weight percent, preferably 18 to 22 weight percent equivalent Al_2O_3 . Furthermore, it should contain enough alkali, such as equivalent Na_2O , to assure complete dissolution of the alumina. The sodium aluminate should exhibit an Na_2O to Al_2O_3 mole ratio in excess of about 1.2, preferably in excess of about 1.35. Of course, for economic and practical reasons, the upper limit of the mole ratio should not be too great so that in practical commercial processes, the ratio will not exceed about 1.5. Impurities, insufficient levels of soda, and high dilutions, will make the sodium aluminate unstable.

Before the start of the process, the reactant solutions are heated to a temperature of 130 to 160°F., preferably to about 140°F. The reaction starts with the nucleation phase in which an initial charge or heel of deionized water is placed in a suitable reactor tank. The water is agitated and heated to a temperature from 140°F. to 170°F. In general, the temperature of the heel is anywhere from 5 to 10°F. below the target temperature at which the reaction is to be run.

An initial charge of aluminum sulfate is added to the water in a very small amount sufficient to adjust the pH of the mixture to a value between 2 and 5, preferably between 3 and about 4. At this point, the concentration of equivalent alumina in the mixture should not exceed about 0.1 weight percent, preferably about 0.05 weight percent. The combination of very low concentration, low pH, and high temperature results in the partial hydrolysis of the aluminum sulfate with the concomitant formation of extremely small crystallites of boehmite. This nucleation process takes place rapidly and the beginning of phase II may start soon after the first addition of aluminum sulfate. However, it is preferred to wait up to

about 10 minutes, preferably about 5 minutes, in order to insure that the nucleation phase has run its course and the system has been properly seeded.

The second phase in the process is carried out by simultaneously adding the sodium aluminate and aluminum sulfate (or other aluminum salt) reactants to the mixture that comprises the water heel containing the crystalline seeds. These solutions are added simultaneously from separate streams into the reactor at preset and essentially constant rates to precipitate the alumina and form an alumina slurry. However, since the reaction is to be carried out at a pH between 7 and 8, the rate of addition of one of the reactants may be slightly adjusted during the run to insure that the desired pH range of the slurry is reached rapidly.

During this phase, the pH will rapidly climb from 2 to 5 to 7 to 8. As the reactants are added to the initial heel, the alumina concentration in the resulting slurry will gradually increase. Under the conditions specified, the precipitate of alumina will tend to crystallize into a Crystalline alumina intermediate boehmite and pseudoboehmite. If the rate of precipitation exceeds the rate of crystallization for the particular conditions used, the excess hydrous alumina will remain in the precipitate as alumina gel (amorphous alumina). The alumina prepared in the present invention exhibits a balance between the amount of crystalline boehmite-pseudoboehmite intermediate and the amount of gel. This requires that the rate of precipitation as dependent on the rate of addition of the reactants, exceeds the rate of crystallization of the hydrous alumina into the boehmite-pseudoboehmite intermediate; excess rate of addition is controlled to leave about 70—85% crystalline alumina and the balance amorphous gel. The pH and temperature of the slurry and the rates of addition of the reactants are maintained during the precipitation to form crystalline boehmite - pseudoboehmite intermediate. Since the rate of crystallization is principally set by the temperature of the system, the rates of addition of the reactants will vary depending on the particular temperature at which the reaction is carried out. On the low temperature side of the operable temperature range, the rate of crystallization will be relatively slow and, consequently, the addition of the reactants should proceed at a slow rate. Generally, the temperature is maintained from 140 to 180°F. For example, for temperatures in the range of 140 to 150°F., the rate of addition should make phase II last in excess of 60 minutes, preferably in excess of 70 minutes.

On the other hand, on the upper side of the operable temperature range, such as 170 to 180°F., the rate of addition can be markedly increased so as to carry out phase II in shorter times, such as 15 to 30 minutes. In the preferred precipitation reaction, the temperature will be between 150 and 170°F. and the rate of precipitation should be controlled so as to carry the reaction over a period of 15 to 70 minutes, generally 30 minutes to 70 minutes, preferably from about 40 minutes to 60 minutes.

In a very specific embodiment, the reaction should be carried out at 155 to 165°F. with the addition of the reactants carried out over a period of 48 to 52 minutes by maintaining the flow of reactants essentially constant over the entire precipitation phase and adjusting the relative flows, if necessary, to provide a programmed pH as follows:

	Time in Minutes From Start of Phase II	pH Range Of Slurry	
	5±2	7.0—7.4	
50	10±2	7.2—7.5	50
	20±2	7.3—7.5	
	50±2	7.35—7.45	

In general, the exothermic nature of the reaction will provide sufficient heat to maintain the temperature at the desired level provided the water heel and reactants are preheated as prescribed. In the event that difficulty is experienced in maintaining a desired temperature, external cooling or heating may be provided to insure appropriate temperature control. Carrying out the precipitation reaction under the prescribed conditions will insure the formation of a precipitated alumina exhibiting the desired balance between crystalline alpha alumina monohydrate (boehmite - pseudoboehmite intermediate) and gel.

At the end of phase II, the concentration of equivalent Al_2O_3 in the slurry should range from 5 to 9 weight percent, preferably from 6 to 8 weight percent.

Material balance of the reactants added to this point may be carried out which will indicate that the ratio of sodium expressed as moles of Na_2O to sulfate ion expressed as moles of equivalent H_2SO_4 will generally be in excess of 0.80, preferably in excess of 0.88, but below 0.97.

At the conclusion of phase II, when the desired quantity of alumina has been precipitated, the flow of aluminum sulfate is stopped. Phase III is then conducted in order to reduce the electrical charge on the surface of the precipitated alumina from a strong positive level to zero or possibly to a low negative value. This is done by adjusting the pH from the value at the end of phase II of 7 to 8 to a value near or slightly in excess of the isoelectric point for alumina, which is somewhere between 9.4 and 9.6. Generally, the pH of the slurry is adjusted to 9.5 to 10.5, preferably 9.6 to 10.0.

The pH change may be done through the use of any strong alkaline solution, such as sodium hydroxide. However, from a practical point of view, it is desirable to continue using as the alkaline solution the initial sodium aluminate reactant solution. By doing so, while the pH change takes place, an additional amount of alumina will be incorporated into the slurry to increase yields and reduce costs. Consequently, in a preferred embodiment of the present invention, phase III is carried out by the continued addition of sodium aluminate at reduced rates. This insures that the pH target is not exceeded or that localized over-concentrations of the sodium aluminate will not cause the precipitation of alumina under high pH conditions favoring the formation of undesirable crystalline phases, such as bayerite (beta alumina trihydrate). During phase III, the temperature of the slurry is maintained and the agitation is continued as during phases I and II. The sodium aluminate is added at a slow rate first continuously until the pH is raised to 9.5 to 10.0 and then discontinuously, if necessary to reach the final pH target. During this phase, the sulfate ion which is fixed onto the surface of the alumina particles is freed as the positive charge of the alumina surface is reduced to zero or made somewhat negative. When a pH from 9.5 to 10.5 is obtained, preferably a pH of 9.6 to 10.0, the flow of sodium aluminate is discontinued and phase III may range from as low as 4 minutes to as long as 20 minutes, preferably it should be carried out over a period of time from about 6 to about 12 minutes.

In phase IV, after all the reactants have been added, the slurry may be aged up to several hours depending on practical considerations such as the readiness of the equipment used in the next steps of filtration and washing. In general, aging for about 30 minutes is used. In any event, since a large batch of alumina slurry prepared through phase III may not be filtered in a single batch, but may be done continuously over a period of time, some of the material will, of necessity, be aged while waiting for the filtration step.

The alumina slurry is then filtered and the filter cake washed to eliminate undesirable impurities. Preferably, deionized water is used as the washing liquid to remove water-soluble impurities. The use of water-containing impurities, for example, calcium, magnesium, chloride, carbonate or bicarbonate, is undesirable. However, depending on the ultimate use of the alumina, some of these impurities such as the volatile impurities may be tolerated. However, metal impurities such as calcium, magnesium, iron, silicon, nickel, etc., cannot be tolerated except in extremely small concentrations.

The term "substantially pure" as used in this specification refers to alumina having levels of impurities expressed on a dry basis that do not exceed the following limits: Sodium expressed as Na_2O , 0.15 weight percent; calcium expressed as CaO , 0.15 weight percent; magnesium expressed as MgO , 0.15 weight percent; silicon expressed as SiO_2 , 0.80 weight percent; iron expressed as Fe_2O_3 , 0.07 weight percent; nickel expressed as NiO , 0.07 weight percent.

The use of deionized water will result in a pure alumina product. The deionized water is usually heated in order to facilitate the removal of electrolytes and may have a temperature of 120 to about 180°F. The removal of electrolytes during washing is facilitated by the crystalline nature of the precipitate. Crystalline materials exhibit a lower tendency to occlude impurities and are easier to wash because of improved filtration characteristics. The amount of deionized water required to achieve good quality in the product may vary depending on the particular filtration equipment used. However, it will normally range from 20 lbs. to 100 lbs. of water per pound of Al_2O_3 (dry basis) in the filter cake.

In certain specific embodiments, the washed filter cake can be used to prepare a satisfactory feed for the preparation of alumina spheroids as described in greater detail hereinafter. This can be done by removing as much water as possible during

the filtration step and using the de-watered filter cake together with specific additives for the preparation of the feed.

In a preferred embodiment, the filter cake is dried to produce a powder of alumina which can be conveniently stored without degrading for long periods of time prior to use in further processing. The drying of the filter cake may be done by several methods, such as tray drying, belt drying, and the like. However, the preferred methods involve the addition of water to the filter cake in order to form a pumpable slurry and the quick removal of water by such methods as spray drying or flash drying. In these cases, the pumpable alumina slurry generally contains 15 to 20 weight percent solids. The slurry is delivered through a nozzle into the drying chamber as finely divided droplets. The droplets come into contact with hot drying gases. For example, in the spray dryer the inlet temperature of the drying gases ranges from 800 to 700°F. The rate of addition of slurry is adjusted so as to obtain an exit temperature of greater than about 250°F., but not to exceed about 400°F., preferably between 300 and 350°F. The use of these conditions insures the partial removal of water without destroying the crystalline nature of the alumina.

In the case where the drying gases are the combustion products of the fuel used, these gases contain substantial concentrations of carbon dioxide. Carbon dioxide upon coming in contact with the alkaline slurry will be absorbed and possibly chemical reacted on the surface. In such cases, the end product will contain a small amount of carbon dioxide as an impurity. This carbon dioxide is not of major concern in most of the steps which follow. However, if conditions so demand, it is possible to reduce the pick-up of carbon dioxide by previously acidifying the pumpable slurry with a trace amount of an acid to a pH of about 7 or lower. Preferred acids in this step are thermally decomposable organic acids, such as acetic and formic acid. Mineral acids may become fixed impurities which will affect the process at a later stage; or, in the case of nitric acid, be a source of undesirable pollutants.

During spray drying, a portion of the gel content of the precipitate may crystallize to the boehmite - pseudoboehmite intermediate depending on specific conditions used. The spray dried produce is not completely dry but contains a certain proportion of water. In general, the spray dried product will contain at least about 18 weight percent water and may range upwards to about 33 weight percent water. Preferably, the range of water content will be between about 20 and about 28 weight percent.

Alumina as used herein refers to an alumina material containing Al_2O_3 , water of hydration, associated water, and the like. The degree of drying of the alumina may be expressed in terms of the weight percent of Al_2O_3 therein. Drying at 1200°C. for 3 hours is considered to produce 100% Al_2O_3 .

The partially dried, hydrous alumina produced by the controlled reaction of sodium aluminate and aluminum sulfate is an intermediate between boehmite and pseudoboehmite. This form of alumina is alpha alumina monohydrate with extra water molecules occluded within the crystal structure and has the formula $Al_2O_3 \cdot xH_2O$ where x is a value greater than 1 and less than 2. The boehmite - pseudoboehmite nature of the product, including its crystalline structure, the degree of crystallinity and average size of the individual crystallites, may be determined by X-ray diffraction techniques.

Pseudoboehmite is discussed by Papee, Tertian and Biais in their paper: "Recherches sur la Constitution des Gels et des Hydrates Cristallises d' Alumine", published in the Bulletin de la Societe Chimique de France 1958, pp. 1301-1310.

Boehmite is a well-defined mineral known for many years whose crystalline nature and X-ray diffraction pattern are given in card No. 5-0190 of the x-ray diffraction index of the American Society for testing Materials.

Other properties which characterize the product of our invention are: its behavior during aging under alkaline conditions; its ability to chemisorb anions such as sulfates at various pH's; its crystalline nature and stability after severe thermal treatments; and the high temperature stability of its surface area, pore volume, and pore size distribution.

All of the above properties stem from the unique balance of crystalline and amorphous gel components in the product combined with its excellent overall chemical purity.

The X-ray diffraction technique employed to determine the degree of crystallinity is as follows: the X-ray diffraction pattern of the product under study is determined using any of the several X-ray diffraction units commercially available, such as a Norelco X-ray diffractometer. A pattern is obtained which gives the

location and intensity of the diffraction peaks. This pattern is compared with the data given in ASTM card No. 5-0190 on boehmite. A matching of all of the diffraction peaks indicates that the product is boehmite. However, if the [020] peak is shifted to 6.6—6.7 Å while the other peaks remain essentially unchanged this indicates the presence of pseudoboehmite. The nature of a product can be further defined by determining the exact position of the [020] d-spacing. Intermediate values of 6.2 to 6.5 Å indicate the presence of materials of intermediate nature. The [020] peak can further be used to determine the degree of crystallinity of the material. The area under this diffraction peak is measured with a planimeter and compared with the area under the corresponding peak of a reference sample run under identical conditions in the X-ray diffractometer. The reference sample is selected from a product known to have a high proportion of boehmite and defined as "100% boehmite". The ratio of the areas provides a relative measure of the degree of crystallinity of the sample under study.

Finally, the nature of the crystallinity can be further detailed by measuring the width of the [020] diffraction peak. Mathematical relationships have been derived by others and published in the literature which allow the calculation of the average crystallite size in Å as a function of the peak width measured half way of the maximum peak intensity.

For a particular diffraction peak, the average crystallite size is inversely related to the width of the peak at half its maximum intensity. Relative measurements can be made by simply measuring the width at half the maximum intensity of the [020] diffraction peak. Large values of the width correspond to small crystallite sizes while small values of the width correspond to large crystallite size. For example, a 100% crystalline alpha alumina monohydrate obtained by the dehydration of well-defined large crystals of alpha alumina trihydrate gives very tall and narrow diffraction peaks. In this material, the [020] reflection occurs at 6.1 Å indicating that the product is boehmite as opposed to pseudoboehmite, and the width at half maximum intensity is only about 0.2 Å indicating the presence of large crystallites.

In contrast, microcrystalline pseudoboehmite exhibits the [020] peak at values ranging from 6.6 to 6.7 Å. These materials show much wider peaks with values at half maximum intensity of about 2 Å or greater. In other words, these materials exhibit a crystalline size approximately one order of magnitude greater than the 100% crystalline alpha alumina monohydrate.

The product of our invention exhibits a structure intermediate that of boehmite and that of pseudoboehmite characterised by a [020]d spacing which ranges from about 6.2 to about 6.4 Å, preferably from about 6.3 to about 6.4 Å. The half maximum intensity width of the [020] peak ranges from about 1.65 to about 1.85 Å, preferably from about 1.75 to about 1.80 Å. This indicates small crystal size, i.e. a crystallite size closer to the micro-size of pseudoboehmite than the macro-size of boehmite.

In terms of relative crystallinity, the product generally has from about 70 to about 85 weight percent of the total amount of Al_2O_3 present in crystalline form, the balance of the alumina being amorphous. The boehmite - pseudoboehmite product of our invention is characterised by high crystalline purity, by small crystallite size—i.e., microcrystallinity and by a high relative degree of crystallinity. These properties can be attributed to its preparation under conditions which give a high ratio of crystalline material to amorphous gel. This is in contrast with materials of the prior art in which the fraction of amorphous gel in the product is either quite high or essentially non-existent such as in boehmite. The intermediate nature of the crystallinity and crystallite size in our material makes it particularly useful in its application as a starting powder for the preparation of catalytic supports of excellent and unexpected properties.

The nature of the balance between crystalline and amorphous materials in our product may be further characterized by the following tests:

- o The conversion of gel components to undesirable crystalline phases, such as bayerite, and
- o Anion surface chemisorption at different pH's.

Amorphous hydrous aluminas have a tendency to crystallize. The particular crystalline phase which is obtained depends on the nature of the environment around the alumina during crystallization. A material consisting of boehmite or pseudoboehmite and containing high proportions of gel components will crystallize to beta trihydrate (bayerite) if exposed to elevated temperatures for long periods of

time in an alkaline aqueous environment. In contrast, materials containing little or no gel components will not develop the bayerite crystalline phase under similar conditions of alkaline aging. For example, an alumina prepared at low temperatures and consisting principally of pseudoboehmite interdispersed with a high proportion of gel will upon aging at least for about 18 hours at about 120°F in a sodium hydroxide aqueous solution of a high pH such as 10, develop bayerite while otherwise remaining essentially unchanged in its crystalline nature. This indicates that the formation of the bayerite is not at the expense or disappearance of pseudoboehmite but that it is formed from the amorphous alumina gel. In contrast, the product of our invention treated under the same conditions will not exhibit the presence of any bayerite. This indicates that the amount of gel in our material is quite small or otherwise more stable.

The anion chemisorption tests involve the preparation of a slurry of the alumina powder to be studied with deionized water, and the potentiometric titration of this slurry with dilute sulfuric acid of known normality over a pH range in which alumina is insoluble. The titration is carried out slowly to make sure that there is ample time for the acid to diffuse into the structure of the alumina product. Over the pH ranges in question from about 9 to about 4 alumina is insoluble, so the titration with sulfuric acid is regarded as a measure of the amount of sulfate which becomes fixed or chemisorbed on the surface of the alumina at a given pH. For different aluminas, the amount of acid required to reach a particular pH from a common starting point, is an indirect measure of the extent of the alumina interface surface exposed to the aqueous medium. Materials which exhibit a very high degree of crystallinity and very large crystallite size possess a small interface surface area and consequently, require small amounts of acid to effect a given change in pH. In contrast, materials which are very high in gel content exhibit high interface surface areas and, consequently, require large amounts of acid to effect the same pH change. Products of intermediate crystalline/gel nature will require intermediate amounts of acid to effect the same pH change.

For example, 100% crystalline alpha alumina monohydrate which consists of very well-defined large crystallites requires only about 53 milliequivalents of sulfuric acid per mole of alumina to change the pH from an initial value of about 8.3 to a final value of about 4.0. In contrast, an alumina prepared at low temperatures in which the pseudoboehmite nature, percent crystallinity and crystallite size indicate a low degree of crystallinity and a high gel content, requires about 219 milliequivalents of sulfuric acid per mole of alumina to effect the same change in pH.

The composition of our invention is characterized by intermediate requirements of sulfuric acid to effect the pH change. From about 130 to about 180 milliequivalents of sulfuric acid per mole of alumina, preferably from about 140 to about 160 milliequivalents, will change the pH of a slurry of our composition from about 8.3 to about 4.0.

The application of the alumina powder product of our invention in making suitable supports for automotive exhaust catalysts requires that the material exhibit good stability of its structural properties at elevated temperatures. For example, its pore volume and surface area, determined after severe thermal treatments simulating those which a catalyst encounters during use, should remain high and stable. These high temperature properties are highly dependent on the purity of the initial material and its structural features as well as the crystalline nature of the product after thermal treatments.

Our material will upon heating lose gradually its water of hydration and other associated or bound water. This dehydration will cause a transition of the crystalline structure to gamma alumina. Further heating to higher temperatures will cause the gamma alumina to convert to delta and eventually to theta alumina. All of these aluminas are transition aluminas of high surface area and pore volume. Heating to still higher temperatures will cause the formation of alpha alumina or corundum which is not a transition alumina and exhibits a very low surface area and pore volume. The final transition to alpha alumina is so profound that its formation is accompanied by dramatic decreases in pore volume and surface area. A good alumina powder capable of conversion to good automotive exhaust catalyst supports should be thermally stable and not exhibit the transition to alpha alumina at moderately high temperatures, such as 1800—1900°F. In general, aluminas with high gel content will have a tendency to sinter to alpha alumina at relatively moderate temperatures, such as 1800—1900°F. Materials which have been prepared at low temperatures and which exhibit high gel content as measured by

several of the tests given in this specification, will show the appearance of undesirable alpha alumina when heated, for example, to 1850°F. for one hour.

In contrast, the product of our invention, which contains only a small amount of amorphous gel, will remain stable and will not show any alpha alumina under identical thermal treatment. Our composition has an X-diffraction pattern of theta alumina, gamma alumina, and delta alumina after heating at about 1850°F for about one hour. Furthermore, the product of our invention will retain at those temperatures very substantial surface areas and pore volumes which will remain stable even for prolonged periods of time under severe thermal treatments.

Our product after a thermal treatment of about 1 hour at about 1850°F., will exhibit a BET nitrogen surface area of about 100 to about 150 square meters per gram, more commonly of about 110 to about 140 square meters per gram. It will also exhibit a nitrogen pore volume from about 0.60 to about 0.75 cm.³/g., most commonly from about 0.64 to about 0.72 cm.³/g.

Furthermore, the pore structure of this thermally treated material will not exhibit a high proportion of microporosity as determined by nitrogen pore size distribution methods. Typically, our product will not exhibit any nitrogen pore volume below about 80Å size, more commonly below 100Å.

Throughout this specification and claims, the "nitrogen pore volume" refers to the pore volume as measured by the techniques described in the article by S. Brunauer, P. Emmett, and E. Teller, *J. Am. Chem. Soc.*, Vol. 60, p. 309 (1938). This method depends on the condensation of nitrogen into the pores, and is effective for measuring pores with pore diameters in the range of 10 to 600Å.

The surface areas referred to throughout this specification and claims are the nitrogen BET surface areas determined by the method also described in the Brunauer, Emmett, and Teller article. The volume of nitrogen adsorbed is related to the surface area per unit weight of the support.

The following Examples further illustrate the present invention.

Example 1

This example illustrates the preparation of an alumina composition of this invention.

Alumina trihydrate was completely dissolved in sodium hydroxide to provide a sodium aluminate solution containing 20 percent Al₂O₃ and having a Na₂O/Al₂O₃ mole ratio of 1.40. 495 grams of water were added to a reaction vessel and then 631 milliliters of 50 percent sodium hydroxide solution were added. This volume of sodium hydroxide solution corresponded to 966 grams at the specific gravity of the solution of 1.53 g./cm.³. The mixture was stirred gently and heated to 200°F. A total of 672 grams of alumina trihydrate was added gradually over a period of 30 minutes. During the addition of the alumina trihydrate, the mixture was heated to a gentle boiling and stirred slowly. Gentle boiling and stirring were then continued for another 60 minutes or until all the trihydrate was dissolved. Heating was stopped and the mixture cooled with stirring to 140°F.

The specific gravity and temperature of the sodium aluminate solution were adjusted to 1.428 g./cm.³ and 130°F. respectively by adding 290 grams of water at a temperature of 140°F. and stirring the mixture. 2016 grams of the solution were used for the preparation of the alumina.

2286 grams of an aluminum sulfate solution containing 7 percent Al₂O₃ and having a specific gravity of 1.27 g./cm.³ at 25°C. and a SO₄⁼/Al₂O₃ mole ratio of 3.01 were prepared by dissolving 1373 grams of aluminum sulfate crystals in 1963 grams of water.

The sodium aluminate solution and the aluminum sulfate solution were heated to 145°F. A heel of 3160 grams of water was placed in a strike tank, the agitator was started, and the heel heated to 155°F.

The heel was acidified to a pH of 3.5 by the addition of 6 milliliters of aluminum sulfate at an addition rate of 36 ml./minute and aged for 5 minutes. At the conclusion of the aging period, the flow of sodium aluminate was started at a rate of 28 ml./minute. Within 5 seconds, the flow of aluminum sulfate was resumed at 36 ml./minute and maintained constant through the 50 minute strike phase. The flow of sodium aluminate was adjusted as needed to maintain the pH of the reaction mixture at 7.4. The strike temperature was maintained at 163°F. by heating the strike tank.

In 50 minutes, all of the aluminum sulfate solution had been added and 317 grams of sodium aluminate remained.

At the conclusion of the strike, the pH of the reaction mixture was increased

to 10.0 by adding 29 more grams of sodium aluminate solution. The final molar ratio of Na_2O to SO_4 was 1.00. The solution was stabilized by aging for 30 minutes at a constant temperature of 163°F.

After aging, the reaction mixture was filtered and washed. For every gram of alumina in the mixture, 50 grams of wash water were used. A standard filtration-wash test was defined as follows. Reaction slurry (600 ml.) was filtered in an 8 inch diameter crock using Retel filter cloth, material no. 80, at 10 inches of vacuum. It was washed with 2.5 liters of water. The filtration time was 2.1 minutes and the filter cake was 7 mm. thick.

The filter cake was reslurried at 15% solids and spray-dried at an outlet temperature of 250°F. to a powder having a total volatiles (T.V.) content of 27.5%, as measured by loss on ignition at 1850°F. The dried powder was calcined at 1850°F. for 1 hour.

The properties of the dry product and the calcined product are shown in Table 1.

TABLE 1

Dry Powder			
Wt. % Na_2O		0.02	
Wt. % SO_4		0.20	
Wt. % T.V.		27.5	
Agglomerate Size		21.5 μ	
Bulk Density		24.1 lbs./ft. ³	
X-Ray Phases		boehmite-pseudoboehmite intermediate —no alpha or beta trihydrate phases present peak for [020] crystallographic plane falls at d spacing of 6.37Å.	
Calcined Powder at 1850°F. For 1 Hour			
N_2 Surface Area		136 m. ² /g.	
N_2 Pore Volume, <600Å total		0.72 cm. ³ /g. 0.95 cm. ³ /g.	
X-Ray Phases		theta alumina, no alpha alumina present	
Pore Size Distribution		A nitrogen PSD measurement showed that all the pores were greater than 100Å diameter and that 50% of the pores were in the 100—200Å diameter range.	

Example 2

Given below in Table 2 is a summary of results of 13 runs using the process conditions described in Example 1.

TABLE 2

Properties	Average	
No. of Runs	13	
Wt. Al_2O_3 /Run (lbs.)	1	
Strike Ratio— $\text{Na}_2\text{O}/\text{SO}_4$	0.93	
Standard Filtration Test (min.)	2.4	
Spray Dried Powder		
Wt. % Na_2O	0.03	
Wt. % SO_4	0.19	
Wt. % T.V.	27.9	
Bulk Density (lbs./ft. ³)	24.0	
N_2 Surface Area at 750°F. for 30 minutes (m. ² /g.)	420	
N_2 Pore Volume at 750°F. for 30 minutes (cm. ³ /g.) <600Å	0.82	
X-Ray	Intermediate Boehmite- Pseudoboehmite	

Calcined Powder at 1850°F. for 1 Hour

Surface Area (m.²/g.)

131

Pore Volume (cm.³/g.)

Total

1.01

<600Å

0.73

X-Ray

Theta alumina, no alpha
alumina present

Example 3

Given below in Table 3 is a summary showing the results for the blended products of six large scale runs. The process was the same as in Example 1 except that 195 lbs. of alumina (dry basis) were made per run. Equipment size and amounts of material were scaled up proportionately. The results were the same as in laboratory scale runs showing that the process could be readily scaled up.

TABLE 3

Spray Dried Powder

W. % Na₂O

0.059

W. % SO₄²⁻

0.31

Wt. % CO₂

1.37

Wt. % T.V.

29.6

Bulk Density (lbs./ft.³)

30.0

N₂ Surface Area at 750°F. (m.²/g.)

413

N₂ Pore Volume at 750°F. (cm.³/g.) <600Å

0.77

X-Ray Phases

Intermediate Boehmite-
Pseudoboehmite

Calcined Powder—1850°F./1 Hr.

N₂ Surface Area (m.²/g.)

131

N₂ Pore Volume (cm.³/g.)

Total

0.97

<600Å

0.70

X-Ray Phases

Theta alumina, no alpha
alumina present

Example 4

The process conditions shown in Example 1 were important to obtain an easily filterable, pure product. In runs where the process conditions of Example 1 were employed except that the reaction temperature and time were varied, the following results were obtained.

TABLE 4

Reaction Temperature	75°F.	120°F.	163°F.
Reaction Time	50 min.	25 min.	50 min. (Example 1)
Standard Filtration Time Test (min.)	2.8	9.0	2.1
Wt. % SO ₄ ²⁻	9.5	0.19	0.20

Thus, a decrease in process temperature led to an increase in sulfate content. A decrease in process time leads to an increase in filtration time.

Example 5

This example illustrates the treatment of a washed alumina filter cake prepared in accordance with the procedure of Example 3 with acetic acid before spray drying. The acetic acid has the effect of decreasing the absorption of carbon dioxide during spray drying. In each run glacial acetic acid was added to the filter cake to a pH of 6.0 and the mixture agitated. The spray dried product contained 3.8 percent acetic acid and 64.5 percent alumina. This represents 0.1 moles of acetate ion for each mole of alumina.

The properties of the alumina products of Example 3 and this Example are shown in Table 7. The carbon dioxide content is 0.76% compared to 1.37% present in the alumina of Example 3.

		TABLE 5		
Spray Dried Powder		Example 3	Example 5	
5	Wt. % Na ₂ O	0.059	0.053	5
	Wt. % SO ₄ ⁼	0.31	0.50	
	Wt. % Solids (Al ₂ O ₃)	63.8	64.5	
	Wt. % CO ₂	1.37	0.76	
	X-Ray	Intermediate Boehmite-Pseudoboehmite	Intermediate Boehmite-Pseudoboehmite	
10	Calcined Powder 1850°F./1 Hr.			10
	N ₂ Surface Area (m. ² /g.)	131	118	
	N ₂ Pore Volume (cm. ³ /g.) <600Å	0.70	—	
	X-Ray	theta alumina, no alpha alumina present	theta alumina, no alpha alumina present	
15				15

Example 6

In order to illustrate the relative proportions of crystalline material and amorphous material in the alumina of this invention, samples of the alumina of Example 1 and aluminas A and B that exhibit lower and higher degrees of crystallinity respectively were slurried with deionized water at Al₂O₃ concentrations of 100 g. Al₂O₃ (dry basis) in one liter of water. Potentiometric titrations of each slurry were slowly conducted at a rate of addition of 1.1 N sulfuric acid of 1 ml./minute over the pH range of 8.3 to 4.0 in which alumina is insoluble.

		TABLE 6			
		Volume of 1.1N H ₂ SO ₄ Solution Required to Reach Indicated pH			
		Example 1	A	B	
30	d [020] spacing midpoint width of peak [020]	6.37Å 1.78Å	6.56Å 1.98Å	6.11Å 0.18Å	30
	pH				
35	8.3	0	0	0	35
	7.0	36	47	14	
	6.0	90	120	25	
	5.0	117	156	36	
	4.0	150	193	47	

The results show that the alumina compositions of this invention required intermediate amounts of acid to effect the same pH change and thus had a gel content intermediate between A and B.

		TABLE 7		
Time/Temperature		4.72 Å Peak Height (mm.)	4.35 Å Peak Height (mm.)	
55	18 hrs./50°C.	8	8	55
	24 hrs./50°C.	11	8	
	41 hrs./50°C.	10	12	
	4 hrs./90°C.	12	14	
	21 hrs./90°C.	18	14	

The degree of crystallinity of the alumina compositions of this invention was further demonstrated by X-ray diffraction measurements of the development of beta alumina trihydrate on alkaline aging and heating. 100 gram samples (dry basis) of alumina A as shown in Table 6 and the alumina prepared in Example 3 as shown in Table 3 were slurried in 250 milliliters of deionized water and brought to pH 10 by the addition of 1N NaOH solution. The time and temperatures of aging and the height of the high and low intensity X-ray peaks of alumina A for beta trihydrate are shown in Table 7. No detectable beta trihydrate was present in the alumina composition of Example 3 under the same conditions of aging and heating as alumina A.

The ease of formation of beta trihydrate under alkaline conditions of Sample A indicated a higher gel content than in the alumina of Example 3.

WHAT WE CLAIM IS:—

- 5 1. An alumina composition comprising a boehmite - pseudoboehmite intermediate, said composition having a [020] d-spacing of about 6.2 to about 6.4Å and requiring from about 130 to 180 milliequivalents of sulfuric acid per mole of alumina to change the pH of a water slurry of the composition from about 8.3 to about 4.0 5
- 10 2. An alumina composition according to claim 1 which possesses a [020] d-spacing of 6.3 to 6.4 Å, a nitrogen pore volume of 0.64 to 0.72 cm³/g and a surface area of 110 to 140 m²/g said pore volume and surface area determined after a thermal treatment for about 1 hour at 1850°F. 10
- 15 3. An alumina composition according to claim 1 or 2 which possesses a mid-point width of the X-ray diffraction peak [020]d of 1.65 to 1.85 Å. 15
4. An alumina composition according to claim 3 which possesses a mid-point width of the X-ray diffraction peak [020] d of 1.75 to 1.80 Å. 15
- 20 5. An alumina composition according to any one of claims 2 to 4 which possesses a nitrogen pore volume of 0.60 to 0.75 cm³/g and a surface area of 100 to 150 m²/g after a thermal treatment for about 1 hour at 1850°F. 20
6. An alumina composition according to any one of claims 1 to 5 in which 140 to 160 milliequivalents of sulfuric acid per mole of alumina will change the pH of a water slurry of the composition from 8.3 to 4.0. 20
7. An alumina composition according to any one of claims 1 to 6 which is substantially pure (as hereinbefore defined). 25
- 25 8. An alumina composition according to claim 1 substantially as hereinbefore described. 25

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